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13. ABSTRACT (Maximum 200 words) The project goals are to investigate the use of unsaturated carbosilanes function alized with a Si-Cl bond in the synthesis of solvent resistant elastomers and high performance polymers. We have successfully synthesized a variety of chlorofunction alized carbosilane polymers which are highly elastic materials. Substitution on this highly elastic backbone with nucleophiles provided materials which were virtually insoluble in every solvent system studied. These solvent resistant materials have shown good thermal stability, being resistant to decomposition in air up to 400 degrees centigrade. <i>DTIC QUALITY INSPECTED 4</i>				
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"The Synthesis and Characterization of Chlorofunctionalized Unsaturated Carbosilane Oligomers and Polymers", J.D. Anderson, S.K. Cummings, J.D. Portmess, and K.B. Wagener, *Polymer Preprints*, **36**(2), 162 (1995).

"Access to Silicon Derived Polymers Via ADMET Chemistry", S. Cummings, D. Smith, and K. Wagener, *Polymer Preprints*, **36**(1), 697, (1995).

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8. **SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT
AND DEGREES AWARDED DURING THIS PERIOD:**

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FINAL PROGRESS REPORT

Description of the research problem studied. Our work is related to the synthesis of a new class of silicon-based solvent resistant elastomers for military use. Such materials require demanding performance such as long-term durability, high solvent resistance, and usefulness over a wide temperature range. Typical applications include hoses, seals, mounting structures, face masks, and binding agents for advance projectile propellants. EMI shielding is also a potential area of use within military electronics.

Summary of the most important results. The project goals are to investigate the use of unsaturated carbosilanes functionalized with a Si-Cl bond in the synthesis of solvent resistant elastomers and high performance polymers. We have successfully synthesized a variety of chlorofunctionalized carbosilane monomers in high purity, which is required for the condensation metathesis polymerization technique used. Both monochloro carbosilane and dichloro carbosilane monomers were synthesized and were shown to be amenable to metathesis polymerization and afforded unsaturated carbosilane oligomers and polymers possessing the Si-Cl bond. The synthesis of this new elastic material consists of essentially two steps whereby the first consists of producing the chloro-functionalized carbosilane backbone, which in fact is highly elastic and reactive. We have successfully synthesized this backbone and characterized it completely with regard to structure, molecular weight, flexibility, and reactivity.

The second reaction consists of substituting on this highly elastic backbone with nucleophiles that will provide the solvent resistance that is sought. Both amine and alkoxide nucleophiles were employed in producing a material that is highly elastic, yet insoluble in virtually every solvent system studied. These solvent resistant materials have shown good thermal stability, being resistant to decomposition in air up to 400 degrees centigrade.

List of all publications and technical reports:

"Acyclic Diene Metathesis in the Preparation of Functionalized Carbosilane Polymers," S. Cummings, J. Anderson, and K. Wagener, *Polymer Preprints*, 37(2), 192 (1996).

"Access to Silicon-Derived Polymers via Acyclic Diene Metathesis Chemistry," S. Cummings, E. Ginsberg, R. Miller, J. Portmess, D. Smith, Jr., K. Wagener, in "Step Growth For High-Performance Materials: New Synthetic Methods," (ACS Symposium Series, No. 624), American Chemical Society, Washington, DC, 1996, Ch. 6.

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Scientific personnel supported by this project and degrees awarded during this period.

S.K. Cummings, 5th Year Graduate Student
J.D. Anderson, Postdoctoral Associate
K. B. Wagener, Professor of Chemistry

Reports of invention by title. None.

Bibliography

1. J. M. Zeigler and F.W. Gordon Fearon, Eds., "Silicon-Based Polymer Science," American Chemical Society, Washington DC, 1990.
2. M. Zeldin, K.J. Wynne, H.R. Allcock, Eds., "Inorganic and Organometallic Polymers (Macromolecules Containing Silicon, Phosphorous and Other Inorganic Elements)"; American Chemical Society: Washington, DC, 1988, and references therein.
3. J.T. Goodwin, Jr., U.S. Patent 2, 607, 791, 1952. W.A. Kriner, *J. Org. Chem.*, 29, 1601 (1964).
4. S. Yajima, *Am. Ceram. Soc. Bull.*, 62, 893 (1983).
5. N.S. Nametkin, V.M. Vdovin, K.S. Pushchevaya, I. Zav'yalov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1453 (1965).
6. H.J. Wu, L.V. Interrante, *Macromolecules*, 25, 1840 (1992).

7. N.S. Nametkin, V.M. Vdovin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1153 (1974).
8. W.P. Weber, X. Zhang, Q. Zhou, R.F. Horvath, T.H. Chan, and G. Manuel, *Macromolecules*, **21**, 1563, (1988).
9. W.P. Weber, Y.T. Park, G. Manuel, *Macromolecules*, **23**, 1911 (1990). W.P. Weber, S.Q. Zhou, *Macromolecules*, **23**, 1915 (1990).
10. H. Lammens, G. Sartori, J. Siffert, and N. Srecher, *J. Polym. Sci., Part B: Polym. Lett.*, **9**, 341 (1971).
11. J.T. Anhaus, V.C. Gibson, W. Clegg, and S.P. Collingwood, *Organometallics*, **12**, 1780, (1993).
12. D.W. Smith "Unsaturated Organosilicon Polymers Via Acyclic Diene Metathesis (ADMET) Condensation Polymerization, Ph.D. Dissertation, University of Florida 1992. K.B. Wagener, D.W. Smith, Jr., *Macromolecules*, **24**, 6073 (1991). D.W. Smith, Jr., K.B. Wagener, *Macromolecules*, **26**, 1633 (1993). D.W. Smith, Jr., K.B. Wagener, *Macromolecules*, **26**, 3533 (1993).
13. S.K. Cummings, D.W. Smith, and K.B. Wagener, *Macromol. Rapid Commun.*, **16**, 347, (1995). J.D. Anderson, S.K. Cummings, J.D. Portmess, and K.B. Wagener, *Polym. Prepr., (Am. Chem. Soc., Div. Polym. Chem.)*, **36**, 162 (1995).
14. S. Cummings, E. Ginsberg, R. Miller, J. Portmess, D. Smith, Jr., K. Wagener in "Step-Growth Polymers For High-Performance Materials: New Synthetic Methods," J.L. Hedrick and J. W. Labadie, Eds., (ACS Symposium Series, No. 624), American Chemical Society, Washington, DC, 1996, Ch. 6.